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TREATMENT OF N-NITROSODIMETHYLAMINE CONTAMINATED WASTE WITH ACT--ETC(U)
JUL 76   M G MACNAUGHTON, T B STAUFFER

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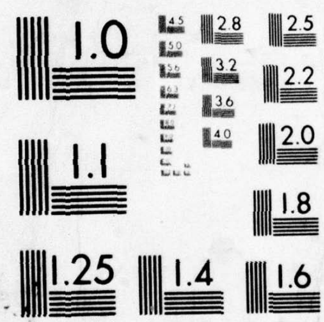

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TREATMENT OF N-NITROSODIMETHYLAMINE CONTAMINATED WASTE WITH ACTIVATED CARBON

ENVIRONMENTAL CHEMISTRY DIVISION
ENVIRONICS DIRECTORATE

JULY 1976

AIR FORCE CIVIL ENGINEERING CENTER
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TYNDALL AIR FORCE BASE
FLORIDA 32403

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Research on the activated carbon removal of N-nitrosodimethylamine (NDMA) from caustic waste solutions generated during the manufacture of UDMH missile fuel is reported. Results indicate that activated carbon will remove NDMA from the caustic solutions without neutralization and three commercial activated carbons all have approximately the same capacities. Although this process is capable of reducing the NDMA concentration in the waste solutions, disposal of the contaminated carbon still remains a problem.

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PREFACE

This technical report was prepared by the Environmental Chemistry Research Division, Air Force Civil Engineering Center operating location location AA, Kirtland Air Force Base, New Mexico. The research was performed under Program Element 63723F, JON 21037C39. Inclusive dates of the research were June 1975 through December 1975. The report was submitted by Major Michael G. MacNaughton and Thomas B. Stauffer.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This report has been reviewed and is approved for publication.

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

SECTION I

INTRODUCTION

During the manufacture of the missile fuel unsymmetrical dimethylhydrazine (UDMH), a caustic waste is produced which contains upwards of 400 mg/liter of N-nitrosodimethylamine (NDMA). This compound has been designated a carcinogen under the Occupational Safety and Health Act. The Environmental Protection Agency (EPA) will not allow disposal of waste containing NDMA in any concentration, except possibly by deep well injection methods. Because of these restrictions on disposal the waste is presently collected at the UDMH production facility in Baltimore MD, and transported by tanker truck to Summerfield NJ for storage.

As a prerequisite to consideration of deep well injection as a viable disposal method for the waste, EPA requested that carbon adsorption be evaluated as a means of reducing the NDMA content prior to shipment from the storage facility to the injection site. In response to the EPA request, and at the behest of the AFLC Aerospace Fuels Directorate (SAALC/SF), the Air Force Civil Engineering Center Operating Location at Kirtland Air Force Base conducted an evaluation of carbon adsorption for removal of NDMA from the contaminated waste. This report summarizes that evaluation.

SECTION II

ACTIVATED CARBON

1. BACKGROUND

The use of activated carbon for the removal of organic compounds from aqueous solutions is a widespread practice. Its applications range from water and waste treatment to decoloring commercial products.

The adsorption of a solute from solution is the result of two driving forces in the system: the insolubility of the solute in the solvent and the affinity of the solute for the solid. Adsorption, in contrast to absorption, is a surface phenomenon and is therefore controlled by interphase reactions. Thermodynamically, adsorption is related to the surface tension of the solvent; any solute that reduces the surface tension of the solvent will be concentrated at the surface. Three kinds of interaction are responsible for the affinity of the solute for the solid: physical, coulombic, and chemical. For many organic molecules, specific chemical bonding is the primary interaction, and this may be designated as specific adsorption in contrast to coulombic adsorption, which is the result of simple electrostatic forces. Physical adsorption is the result of short range Van der Waals forces where the adsorbed molecule is not affixed to any particular site.

Mathematically, adsorption is usually expressed as an adsorption isotherm. In this expression the distribution of the solute between the solid and solvent is given as a function of the solute-solvent-solid system. The Langmuir adsorption isotherm is one model which has been used to express single layer adsorption reactions. This model is based on the assumptions that maximum adsorption corresponds to a saturated monolayer on the surface of the solid and that the energy of adsorption is constant. The Langmuir isotherm is given by:

$$\Gamma = \frac{\max \cdot KC}{(1 + KC)} \qquad (1)$$

where Γ is the amount of solute adsorbed per unit

weight or area of solid, max is the amount of solute per unit weight or area which forms a monolayer on the surface, C is the concentration of the solute in solution at equilibrium, and K is a constant which is a measure of the adsorption energy. A more convenient form of Equation 1 is:

$$\frac{C}{\Gamma} = \frac{1}{K\Gamma max} + \frac{C}{\Gamma max} \qquad (2)$$

which allows the data to be presented in a linear form and the adsorption energy (K) and the saturation surface coverage (Γmax) to be determined. K and Γmax are a measure of those characteristics of the adsorbent (surface area, surface functional groups, etc.) which directly determine the efficiency of removal of the solute from solution. Activated carbon has been used extensively for removal of organic solutes because of its high surface area and the high affinity of many organic materials for the surface sites of this substrate.

2. EXPERIMENTAL

a. Materials and Reagents

Carbons used for these studies were purchased from the appropriate manufacturers and were chosen because of their availability, cost, and general use.

All reagents were ACS reagent grade or better. N-nitrosodimethylamine was 99 percent pure, manufactured by Aldrich Chemical Company, and supplied by the USAF Environmental Health Laboratory at Kelly Air Force Base. The caustic NDMA solution used in the studies was obtained in a 55-gallon drum and was the waste product of the FMC plant in Baltimore MD. It was considered to be representative of the waste stored in Summerfield NJ. The 55-gallon drum was stored outdoors and required volumes were withdrawn using a syphon. The concentration of the sample volumes varied between 220 and 190 mg/liter due to stratification in the drum and volatilization; the actual sample concentration was measured prior to each experiment.

b. Experimental Procedure

Adsorption studies were performed using two techniques. Experiments designed to determine the maximum

surface coverage (Γmax) for varying pHs and with different carbons were performed in a batch mode. Varying surface coverages were achieved by adding different amounts of the carbon being studied to 25 ml of the NDMA solution in 35 ml centrifuge tubes. The tubes were sealed with Teflon-lined caps and rotated end-over-end for 24 hours at 10 rpm. The temperature was not controlled but was 22 $\pm$ 2°C throughout the experiments. After equilibration the tubes were centrifuged and known volumes of the solution were removed for analysis.

For those studies designed to measure breakthrough, a columnar mode was utilized. A 9 mm pyrex tube (0.62 cm^2 in cross-sectional area) with an all-glass flow valve at the exit was used as the column. A 1-liter storage reservoir maintained the head above the column.

c. Analysis

All analyses for NDMA were performed on a Tracor MT 222 gas chromatograph using a flame ionization detector and a 6 foot by 1/4 inch Porapak Q column. The oven was operated isothermally at 170°C and the inlet and detector were maintained at 250°C. The detection limit was 0.5 mg/liter using a 3μl injection.

To reduce tailing and column bleed, the samples were distilled before analysis to preclude injection of the caustic solutions. Greater than 97 percent recovery of a 5 mg/liter solution was achieved in a test of the distillation procedure.

3. RESULTS

a. Effect of pH

Although the waste itself consists of approximately 20 to 25 percent sodium hydroxide, the caustic could be neutralized if such action would lead to greater removal efficiencies. To the contrary, Figure 1 shows that the greatest removal is achieved at the highest pH. This may be due to the lower solubility of the NDMA in the caustic solutions since the same effect on volatilization was observed in the evaporation studies reported earlier[1]. Figure 2 illustrates the effect of pH on

[1]MacNaughton, M. G., "The Evaporation and Degradation of N-nitrosodimethylamine in Aqueous Solution," AFCEC-TR-75-9, 1975.

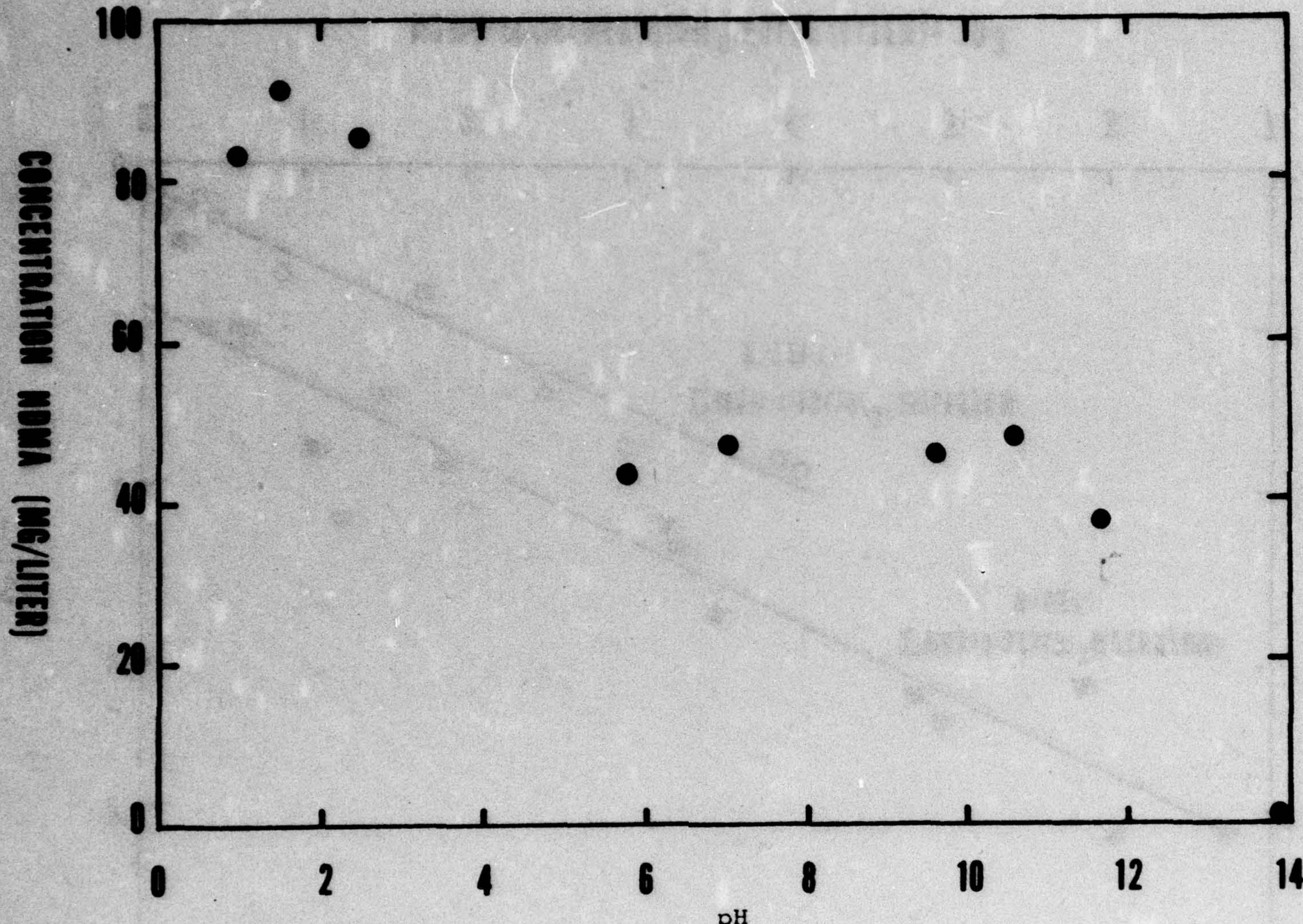

Figure 1. Final NDMA concentration as a function of pH. 20 gm Filtrasorb 400, initial NDMA concentration - 500 mg/l, equilibration time - 2 hours.

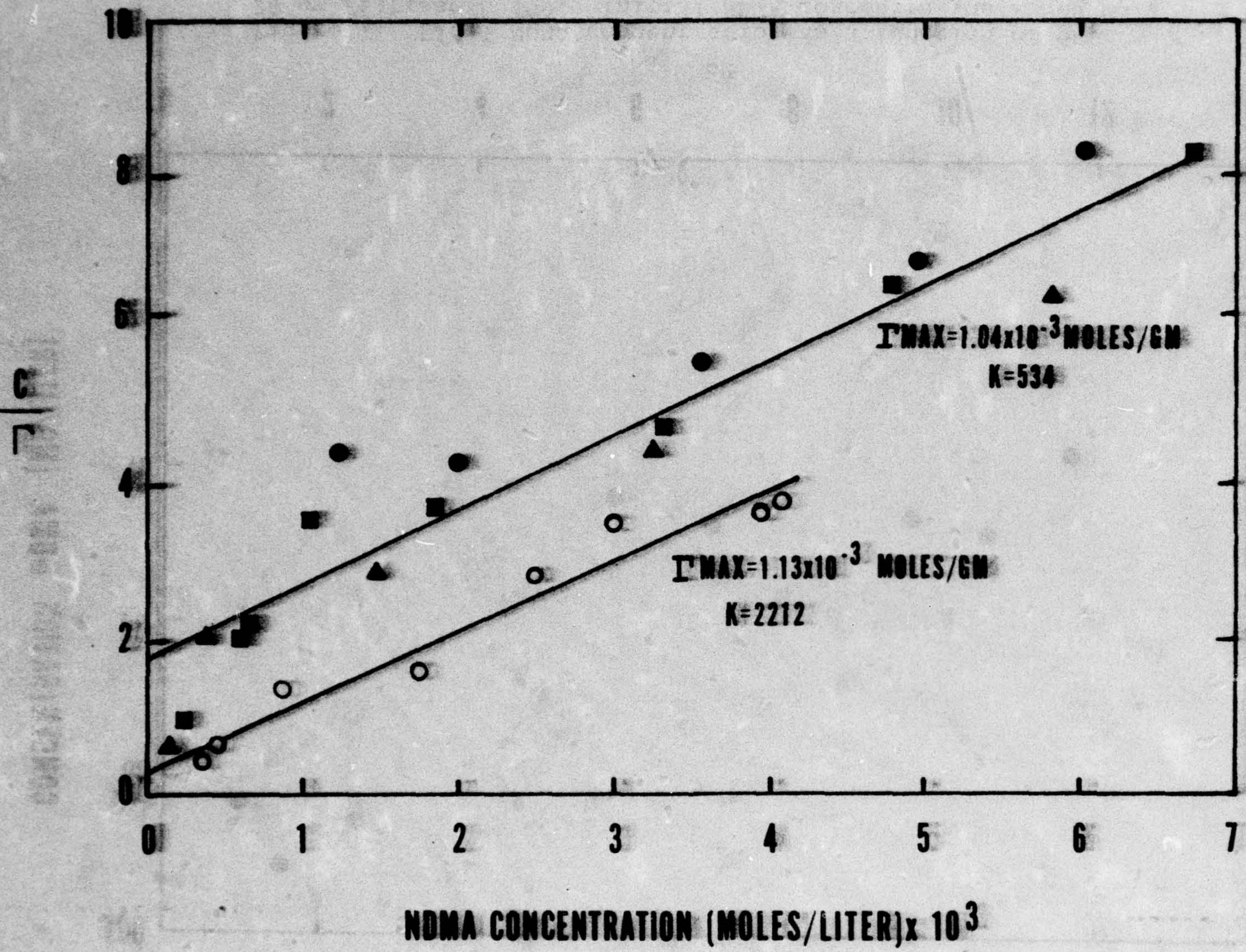

Figure 2. Langmuir plot of NDMA adsorption as a function of pH. (●) pH<4.0, (▲) $4.0 \leq pH \leq 10$, (■) 10>pH>12, (O) 20 percent NaOH.

calculated monolayer coverage and the adsorption energy as described in Section I. As can be seen, the maximum monolayer coverage (Γmax) and therefore the size of the adsorbing molecule is approximately the same for all pHs studied. In a 20 percent caustic solution the adsorption energy (k) is substantially higher.

The above results indicate it is not advisable to neutralize the waste prior to treatment with activated carbon. In fact, the less the waste is diluted the better the adsorption efficiency becomes. Not neutralizing the caustic will also reduce the chance of volatilizing the NDMA.

Figures 3 a, b, and c show that the different carbons have approximately the same capacity; 1.42×10^{-3} moles/gm were measured for Nuchar 12 x 40 (Westvaco Corporation) and Westvaco 8 x 30, respectively, as compared to 2.37×10^{-3} moles/gm for the Calgon Filtrasorb 400.

b. Effect of Volume Treated

Figure 4 shows the NDMA concentration in the effluent of the carbon column versus the volume of the caustic waste treated. After a waste volume of approximately 3.5 liters (0.23 liters/gm carbon), there is a significant increase in the observed concentration of the effluent. This is equivalent to a loading of 45 gm NDMA per Kgm carbon (0.6×10^{-3} mole/gm). Based on this loading and a waste production of 4000 gal/day, treatment would require 16.5 gms (0.036 lb) of carbon per gallon of waste--approximately 150 lbs per day. Use of a single column is not the most efficient method of reducing the NDMA to acceptable levels, since most of the capacity of the carbon is still unused after the effluent has a significant NDMA concentration. By using two or more columns in series, the full capacity of the carbon is usable to a much greater extent. In Figure 4 this would increase the volume that could be treated from 0.23 liters/gm (28 gal/lb) to approximately 0.67 liters/gm (81 gal/lb).

In addition to the actual volume of waste treated, the rate at which the waste is applied is also a factor in system performance. Figure 5 shows that decreasing the flowrate by a factor of three delays the breakthrough of the NDMA until approximately 1.5 times more waste has

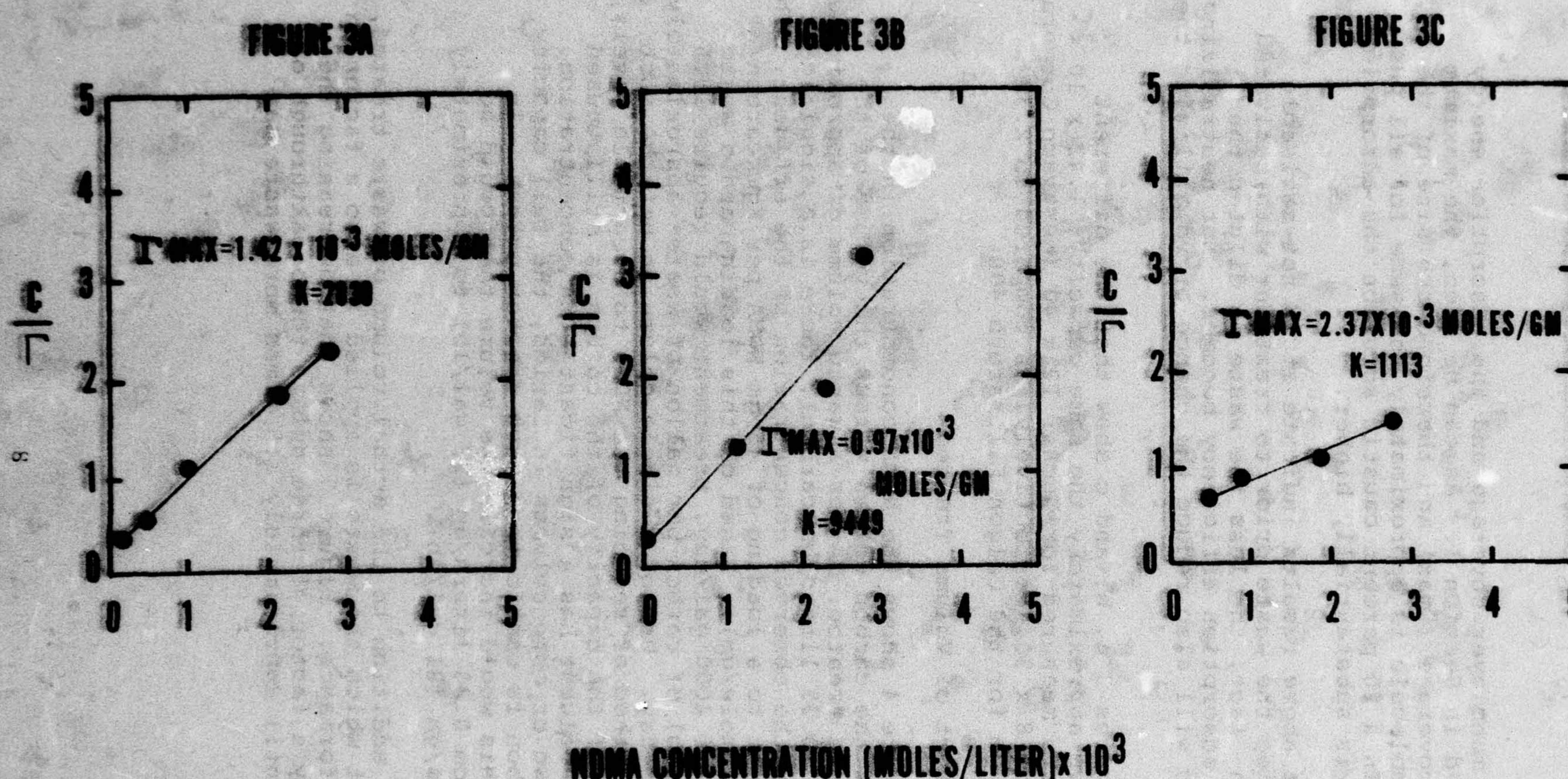

Figure 3. Langmuir plots of NDMA adsorption on different activated carbons.
a. Nuchar 12 x 40, b. Westvaco 8 x 30, c. Filtrasorb 400.

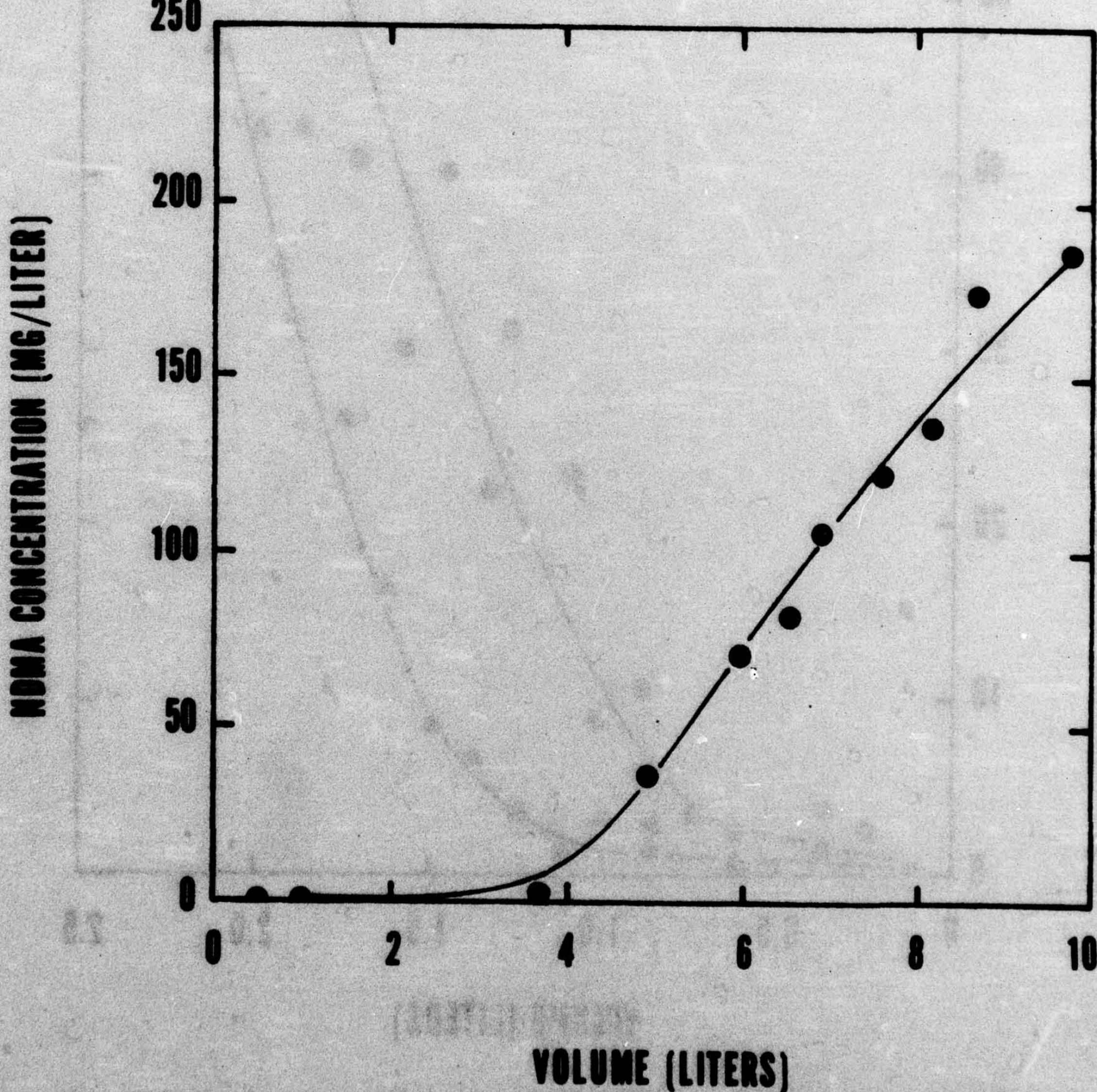

Figure 4. Residual NDMA concentration as a function of volume of caustic waste treated in a columnar mode. 15 gm Filtrasorb 400, flowrate - 0.6 liter/Kgm.min, initial NDMA concentration 193 mg/liter.

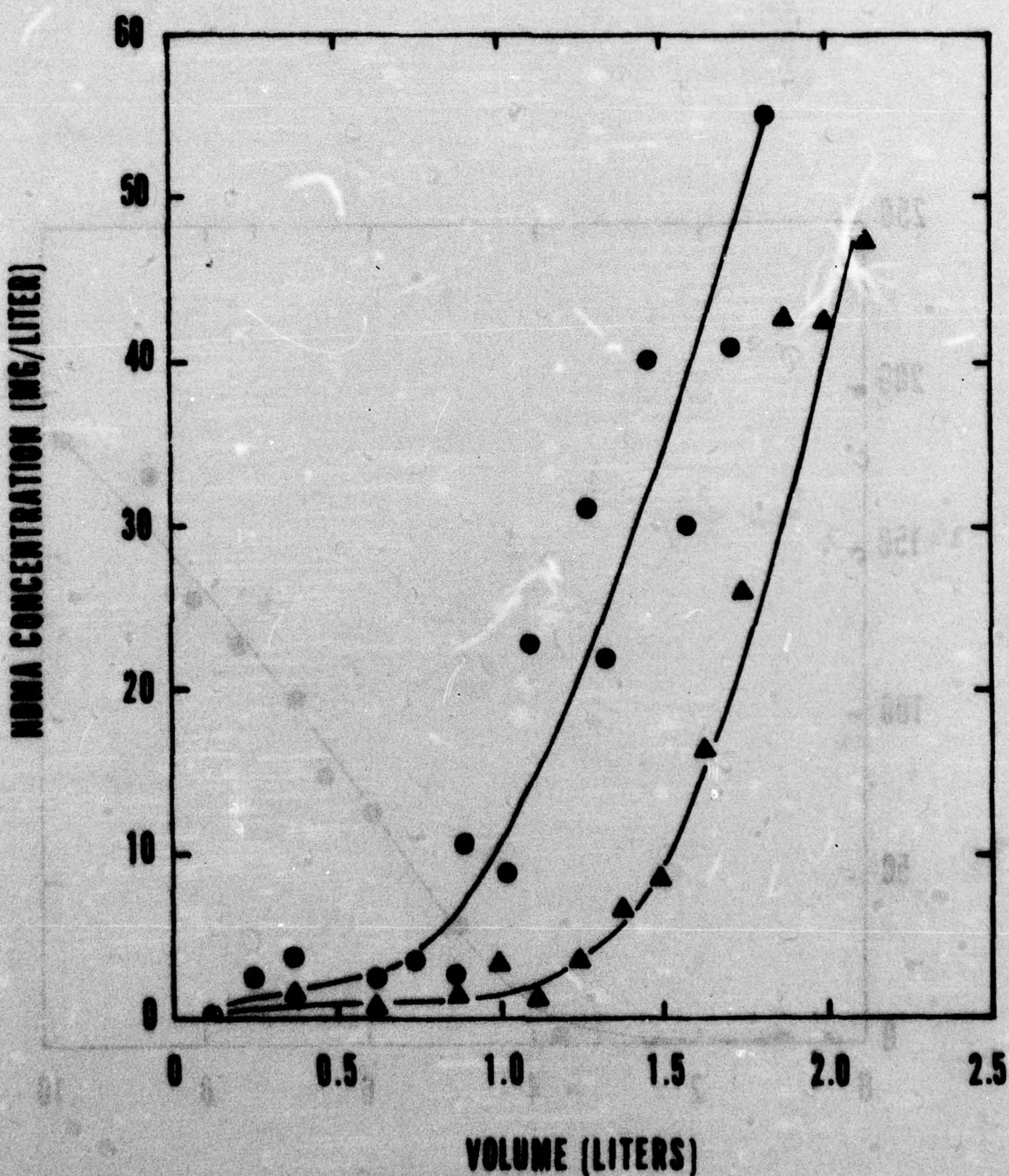

Figure 5. Residual NDMA concentration as a function of flowrate and volume treated. 5 gm Filtrasorb 400, initial NDMA concentration - 213 mg/liter. (●) 0.6 liters/Kgm.min, (▲) 0.2 liters/Kgm.min.

passed through the column. It must be noted that the system used here is not representative of the normal commercial installations, and the flowrate used would depend on the specifications of a particular manufacturer's equipment.

c. Regeneration of Carbon

Any discussion of waste treatment using carbon adsorption must address the ultimate disposal of the contaminants subsequent to their uptake by the carbon. Carbon adsorption merely concentrates the contaminants and does little to reduce the problem of disposal under the restrictions established by the Environmental Protection Agency. In conventional uses of activated carbon, thermal regeneration or destruction is a common solution. The high sodium content of the caustic waste presents a problem in using any thermal methods, since the combustion of a high sodium waste is claimed to cause damage to furnace refractory material. Because the carbon absorbs some of the sodium hydroxide from the waste, a simple distilled water rinse was used to see if the sodium content could be reduced without removing the adsorbed NDMA. Figure 6 shows the resulting pH of the rinse water during this attempt. After 3.5 liters of distilled water (1.17 liters/mg) had passed through the bed and the pH indicated the hydroxide had been removed, the sodium content of the carbon was 0.4 gm/Kgm. It is not known what impact this sodium concentration would have on refractory linings. This may be a moot question, however, since the last of the distilled water rinse had an NDMA concentration of 7 mg/lit, indicating that the NDMA was being desorbed from the carbon by the distilled water.

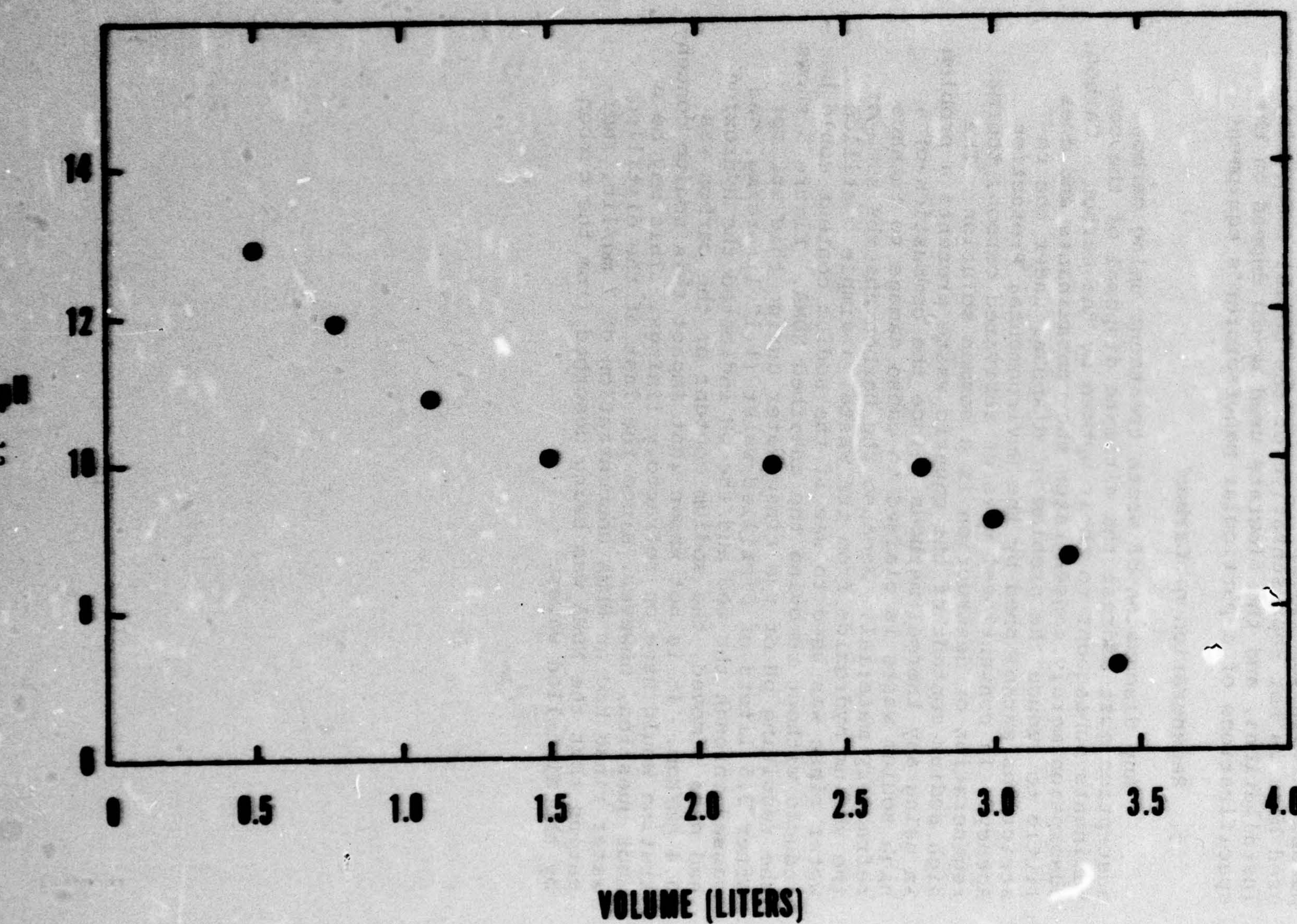

Figure 6. pH of distilled water rinse as a function of volume passed through the column. 3.0 gm Filtrasorb 400 after being exhausted with caustic waste.

SECTION III

SUMMARY AND CONCLUSIONS

Based on the results reported here it is not recommended that carbon adsorption be used to treat the NDMA-contaminated waste at Summerfield NJ. Although the three carbons tested are capable of reducing the NDMA concentration in the waste by more than 99 percent, the position of the EPA in restricting disposal of any liquid waste which contains NDMA at any concentration precludes this technique. In addition, disposal of the contaminated carbon could also pose serious problems unless a sufficiently corrosion-resistant incinerator can be found. If such an incinerator becomes available, and if deep well injection is approved, then carbon adsorption could be a viable process for reducing the NDMA concentration in the waste prior to shipment and injection.

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